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Modular Functionalization of Carbon Nanotubes and Fullerenes

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Abstract: A series of highly efficient, modular zwitterion-mediated transformations have been developed which enable diverse functionalization of carbon nanotubes (CNTs, both single-walled and multi-walled) and fullerenes. Three functionalization strategies are demonstrated. (1) Trapping the charged zwitterion intermediate with added nucleophiles allows a variety of functional groups to be installed on the fullerenes and carbon nanotubes in a one-pot reaction. (2) Varying the electrophile from dimethyl acetylenedicarboxylate to other disubstituted esters provides CNTs functionalized with chloroethyl, allyl, and propargyl groups, which can further undergo S_N2 substitution, thiol addition, or 1,3-dipolar cycloaddition reactions. (3) Postfunctionalization transformations on the cyclopentenones (e.g., demethylation and saponification) of the CNTs lead to demethylated or hydrolyzed products, with high solubility in water (1.2 mg/mL for MWCNTs). CNT aqueous dispersions of the latter derivatives are stable for months and have been successfully utilized in preparation of CNT-poly(ethylene oxide) nanocomposite via electrospinning. Large-scale MWCNT (10 g) functionalization has also been demonstrated to show the scalability of the zwitterion reaction. In total we present a detailed account of diverse CNT functionalization under mild conditions (60 °C, no strong acids/bases, or high pressure) and with high efficiency (1 functional group per 10 carbon atoms for SWCNTs), which expand the utility of these materials.

Introduction

Carbon nanotubes (CNTs) have emerged as central building blocks in nanoscience as a result of their unique mechanical, geometric, thermal, and electrical properties.[1−5] With aspect ratios that can reach over 1000, CNTs are envisioned to be an ideal material for the fabrication of composites with ultimate performance. Despite this great promise, many real applications of CNTs have been impeded by difficulties associated with their processing and manipulation. Carbon nanotubes are difficult to disperse, largely due to the intrinsic strong intertube van der Waals interactions. This has led to many different CNT covalent functionalization processes in schemes that usually require relatively harsh conditions,[6−11] such as high reaction temperatures (130−150 °C), high pressure (1.3 GPa), long reaction times (up to 120 h), and/or highly active reagents (e.g., concd H_2SO_4, concd HNO_3, lithium diisopropylamide (LDA)), which are incompatible with many functional groups. To further CNT applications the development of alternative, more accommodating, functionalization schemes are desired. We recently discovered that C_{60} and single-walled carbon nanotubes (SWCNT) can be functionalized with high efficiency through reactions initiated by a zwitterionic complex between dimethyl acetylenedicarboxylate (DMAD) and 4-dimethylaminopyridine (DMAP).[12] The proposed reaction mechanism, shown for C_{60} in Scheme 1, formally involves addition of the zwitterion intermediates to

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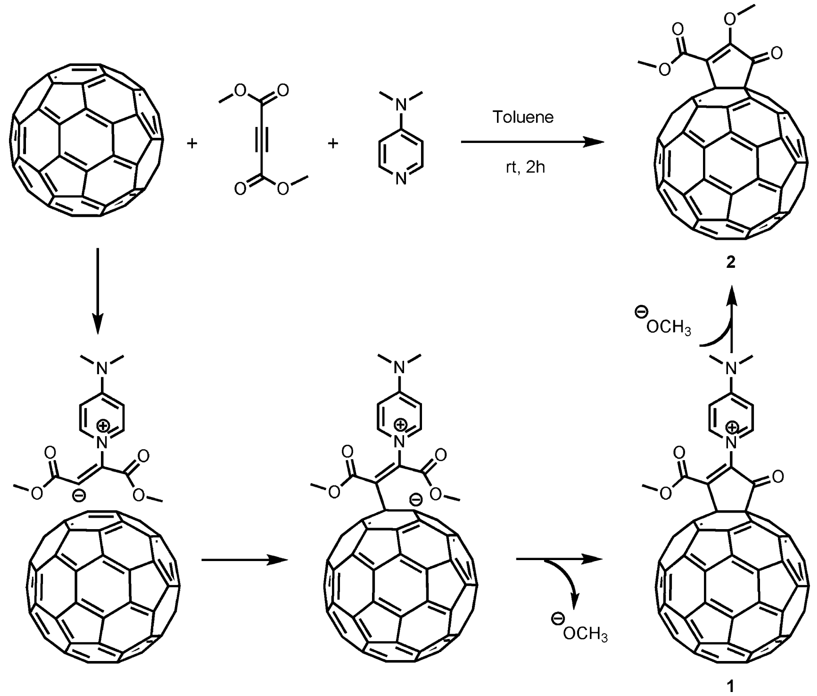
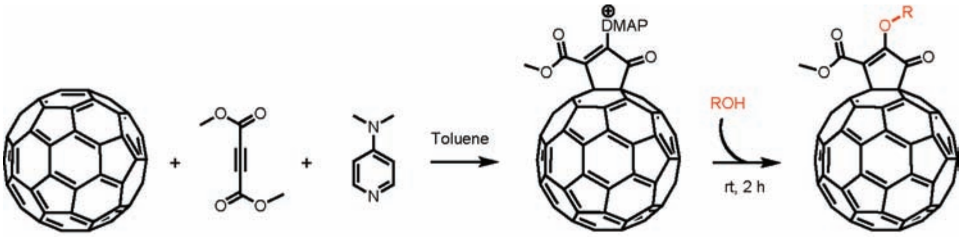
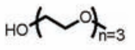
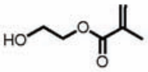
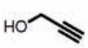
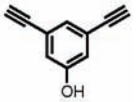
10.1021/ja810049z CCC: $40.75

Scheme 1. Reaction Pathway in the Zwitterion-Mediated Fullerene/CNT Functionalization



Scheme 2. Functionalization of Fullerene with Trapping Charged Intermediate Approach



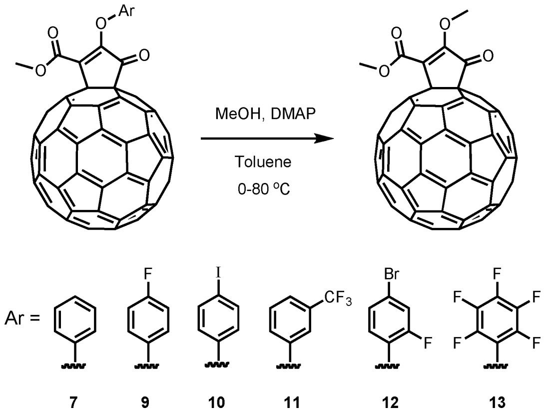
Product	3	4	5	6	7	8
ROH						
Yield %	55	52	57	61	46	52

electrophilic fullerene/CNT double bonds, followed by back attack of the fullerene/CNT centered anion on the carbonyl carbon of the ester group to afford a charged intermediate **1**. In the final step, the DMAP moiety was replaced with a methoxy group, providing the fullerene/CNT-DMAD adduct **2**. The charged intermediate **1** can be trapped with other nucleophiles, leading to the formation of adducts with different functional groups on the vinyl position.[12] In this report, we show that a novel, pentafluorophenoxy-substituted fullerene derivative, prepared through trapping of the charged intermediate approach, serves as a well-defined precursor for modular fullerene functionalization. Additionally diester-based acetylene electrophiles can be used to introduce a variety of functional groups for further elaboration of fullerenes/CNTs. We also demonstrate that this method can be applied to large-scale functionalization of multiwalled carbon nanotube (MWCNTs) and that water dispersible CNTs can be prepared by hydrolysis and demethylation reactions.

Results and Discussion

Trapping Charged Intermediate with Nucleophiles in a One-Pot Reaction. On the basis of the reaction mechanism proposed in Scheme 1, the straightforward approach for CNT and fullerene functionalization is nucleophilic trapping of **1** leading to various substitutions on the vinyl position. We previously demonstrated that simple aliphatic alcohols are suitable nucleophiles if added in excess during CNT/fullerene functionalization.[12] To further explore the scope of this approach, we investigated reactions of C_{60} with triethylene glycol monomethyl ether, hydroxyethylmethacrylate, and propargyl alcohol (**3**−**6** in Scheme 2). In all cases, monofunctional fullerene derivatives were obtained in good yields. We also found that phenol moieties, with or without substitution can also be installed on the vinyl position (e.g., **7** and **8** in Scheme 2). The phenoxy-substituted fullerene derivatives attracted our attention as substrates capable of undergoing subsequent substitution reactions on the vinyl position of the cyclopenten-

Scheme 3. Substitution Reaction of Phenoxy-Functionalized Fullerenes with Methanol



one. Introducing electron-withdrawing groups on the phenyl ring would make for a better phenoxide leaving-group, and to obtain the best precursor, we tested fullerene derivatives substituted with various electron-deficient phenoxy moieties (Scheme 3). Our standard procedure[12,13] yielded a series of phenoxy-functionalized fullerene derivatives (**7**, **9**−**13**). The phenols used to effect this functionalization were chosen on the basis of their pK_a values, which range between 5.53 (pentafluorophenol) and 9.99 (phenol). Higher pK_a values presumably correspond to higher nucleophilicity, but lower pK_a values will produce a more substitutionally labile product.

With the phenoxy-substituted fullerene derivatives in hand, substitution reactions with methanol as the nucleophile were studied (Scheme 3). All the reactions were conducted in the presence of a large excess (300 equiv) of methanol and a stoichiometric amount[14] of DMAP in toluene and the reaction progress was monitored by thin layer chromatography.[15] The reactions were started at room temperature (at 0 °C in the case of pentafluorophenoxy-derivative **13**) and subsequently heated to 80 °C by increasing the temperature by 15 °C every 3 h. The reaction with compound **13** showed product formation at 0 °C and went to completion after stirring at room temperature for 8 h. The reactions with 2-fluoro-4-bromophenyl derivative, **12**, and *m*-trifluoromethylphenyl derivative, **11**, showed conversion at 35 and 50 °C, respectively. The reactions with the other three derivatives, 4-iodophenyl-, 4-fluorophenyl, and phenyl-substituted fullerenes (**7**, **9**, and **10**, respectively) did not show any conversion until raising the temperature to 65 °C.[15] On the basis of this analysis, compound **13** showed the highest substitution reactivity and its utilization for fullerene functionalization has the following advantages: (1) The starting material **13** is highly soluble in a variety of solvents (e.g., toluene, THF, dichloromethane, etc.) in contrast to pristine fullerenes that only display useful solubility in aromatic solvents. Derivative **13** also shows good stability and is insensitive to oxygen and moisture. (2) The substitution reaction occurs under mild conditions (room temperature, with catalytic amount of DMAP loading). (3) Substitution reactions with **13** proceed cleanly with almost quantitative conversions. (4) The substitution reaction shows general substrate scope and a variety of alcohols can be installed (e.g., pentanol, triethylene glycol monomethyl ether, 5−10 equiv). Considering these advantages, **13** opens new possibilities for fullerene functionalization and facilitates its applications.

Scheme 4. Substitution of Charged DMAP Moiety by Electron-Deficient Phenol vs Competitive Methoxide Back-Attack Side Reaction

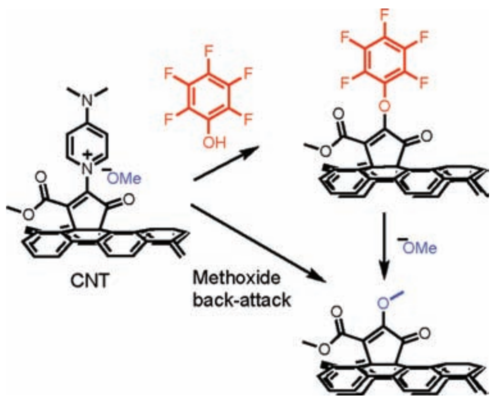
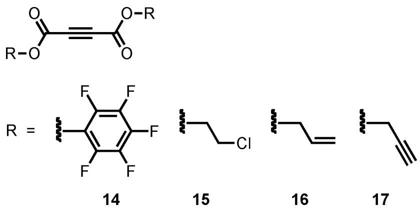


Chart 1. Acetylenedicarboxylate-Based Electrophiles



In spite of our success in modular fullerene functionalization via a well-defined precursor (i.e., **13**), extending this strategy to SWCNTs turned out to be a challenging task, which is likely due to the propensity of attack by methoxide generated during the reaction. The elevated temperatures and longer reaction time required for CNT functionalization (60 °C, 36 h for SWCNTs), are sufficient for DMAP-catalyzed methoxide substitution even if the pentafluorophenoxy product is produced (Scheme 4).

Zwitterionic Reactions with Functionalized Substrates. As illustrated in Scheme 1 for CNTs, in the absence of added nucleophiles the methoxy group displaced from the ester of dimethyl-acetylenedicarboxylate ends up attached to the central alkene carbon. We reasoned that using related electrophiles could provide an efficient strategy enabling high-density functionalization of SWCNTs with target functional groups. In this way the functional groups will be attached to the alkene and the ester groups in the addition product.

We were particularly interested to produce dipentafluorophenyl acetylenedicarboxylate **14** as the electrophile (Chart 1) in an

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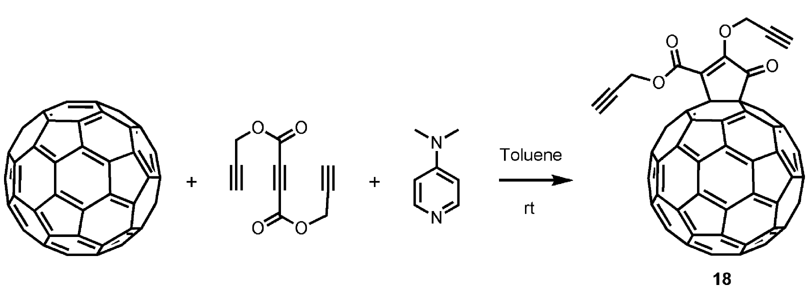
(13) Addition of pentafluorophenol in the beginning of the reaction only led to very low conversion even at 60 °C. Presumably, the acidic phenol protonated the DMAP and/or the zwitterion intermediate, thus significantly decreasing their nucleophilicity. Therefore, it is necessary to add the nucleophiles, especially those with acidic protons, after the cyclopentenone moiety has been installed on the fullerene (refer to Experimental Section for procedure details). Also, the DMAP-substituted fullerene zwitterion intermediate (**1**) seems to have a lifetime of couple of hours, and the DMAP moiety is not replaced immediately by methoxide under these conditions. Before phenol addition, a large amount of precipitates (presumably the cationic intermediate) can be observed for several hours. However, upon addition of nucleophiles (alcohol or phenol), within ∼1 h, the solution becomes homogeneous again, which is likely due to the conversion of cationic intermediate into the neutral substituted product. Attempted characterization of the precipitate failed due to its extremely poor solubility.

(14) Catalytic loading of DMAP was also tested in later studies and showed similar results.

(15) In a second study the crude reaction mixtures were also analyzed by ^{1}H NMR to obtain more quantitative data (ratio of starting material to product) for the substitution reaction. The results (Table S1) showed a correlation between the pK_a values of the phenols and the reactivity of the corresponding phenol-fullerene adducts.

Scheme 5. Functionalization of Fullerene with Dipropargyl Ester



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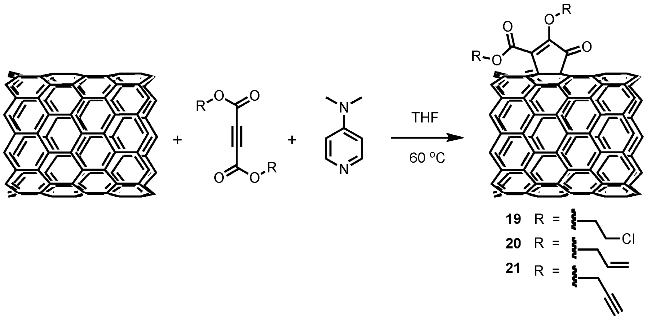
Scheme 6. Functionalization of CNTs with Acetylenedicarboxylate Electrophiles



attempt to introduce reactive electron-deficient phenol moieties onto SWCNT surface. However, the synthesis of **14** is nontrivial,[16] and we only succeeded in isolating trace amounts of the target compound. As a result we turned our attention to alkyl halide, allyl, and propargyl groups, based on their capability of undergoing further chemical transformations, such as S_N2 substitution,[17] cross coupling,[18,19] thiol addition,[20] olefin metathesis,[21,22] or 1,3-dipolar cycloaddition (click chemistry).[23] The preparation of the diester acetylenedicarboxylate incorporating these latter functionalities is convenient,[24] and the electrophiles **15**−**17** (Chart 1) were synthesized on 10 g scale in high yield (88−91%). Under standard reaction conditions[12] with the dipropargyl ester as the electrophile (Scheme 5), fullerene derivative **18** was obtained in an isolated yield of 45%.[25] The product structure was confirmed by NMR and MALDI-MS characterization.

Encouraged by the successful C_{60} model study result, SWCNT functionalization with **15**−**17** was then pursued using conditions that were effective for DMAD (Scheme 6).[26] The purified products were characterized by Raman spectroscopy, and SWCNT derivative **19** shows the expected increase of the D-band (or disorder mode) at 1293 cm^{-1} relative to the starting SWCNT (Figure 1a), thereby indicating a significant conversion of SWCNT sp^2 carbons to sp^3 centers.[27] Addition reactions are also confirmed by UV−vis−NIR absorption spectroscopy (Figure 1b), and functionalization results in the reduction of the interband transitions between van Hove singularities that are characteristic of pristine HiPCO nanotubes. This latter aspect indicates a disruption of the extended π-network by the conversion of sp^2- to sp^3-hybridized carbon atoms.[28,29] Further evidence for functionalization of SWCNTs was obtained from the X-ray photoelectron spectroscopy of **19** (XPS, Figure 1c), which displays significant signals for carbon, oxygen, and chlorine atoms. The peaks at 197, 270, 283, and 530 eV correspond to the chlorine 2p and 2s, carbon, and oxygen 1s core-level energy. From the chlorine-to-carbon ratio (13%), we calculated the degree of coverage of about one functional group for 7.2 carbon atoms. This degree of functionalization density was confirmed by thermogravimetric analysis (TGA) with **19** displaying a weight loss of 70% (compared to pristine SWCNTs, Figure 1d). This loss corresponds to 1 functional group for 8.5 carbon atoms, in accord with XPS result. Infrared spectroscopy (Figure 2) of **21** revealed absorption signals assigned to the carbonyl group at 1730 cm^{-1} and the weak signals at 2130 and 3260 cm^{-1} are attributed to the C≡C stretching and sp C−H stretching modes, respectively. These features are consistent with the dipropargyl ester adduct structure. Correlations with the C_{60} model systems support that the SWCNT reacts with these functional acetylenedicarboxylate esters **15**−**17** in a similar fashion as observed when DMAD is used as the electrophile.

To demonstrate the utility of functionalized SWCNTs we initially used the dichloroethyl-substituted SWCNT, **19**, as the starting material for reaction with 4-fluorophenol through simple S_N2 substitution.[17] This reaction was conducted in ethanol at 90 °C for 12 h, with potassium carbonate and 1-methylimidazole as the base (Scheme 7a).[30] The purified SWCNT product **22** was characterized by XPS (Figure 3), which revealed a decreased Cl signal and a new F signal. On the basis of the ratio of Cl and F signals, the functionalization density of the phenol moieties was estimated to be one phenol for 15 SWCNT surface carbon atoms. To demonstrate diallyl-substituted SWCNT **20** as a reaction precursor (thiol addition[20]), reaction of **20** with 1-hexylthiol in THF under Ar atmosphere and UV irradiation (254 nm) was conducted for 18 h (Scheme 7b). The purified

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(25) Unreacted fullerene (26%) was recovered. Some di-adduct and tri-adduct were observed on MALDI-MS of the crude product, which is similar to the case of compound **2** preparation.

(26) Preparation of SWCNT derivatives **19**−**21** followed the same general procedure as we previously reported (ref 12). Also see the procedure for synthesis of **19** in the Supporting Information.

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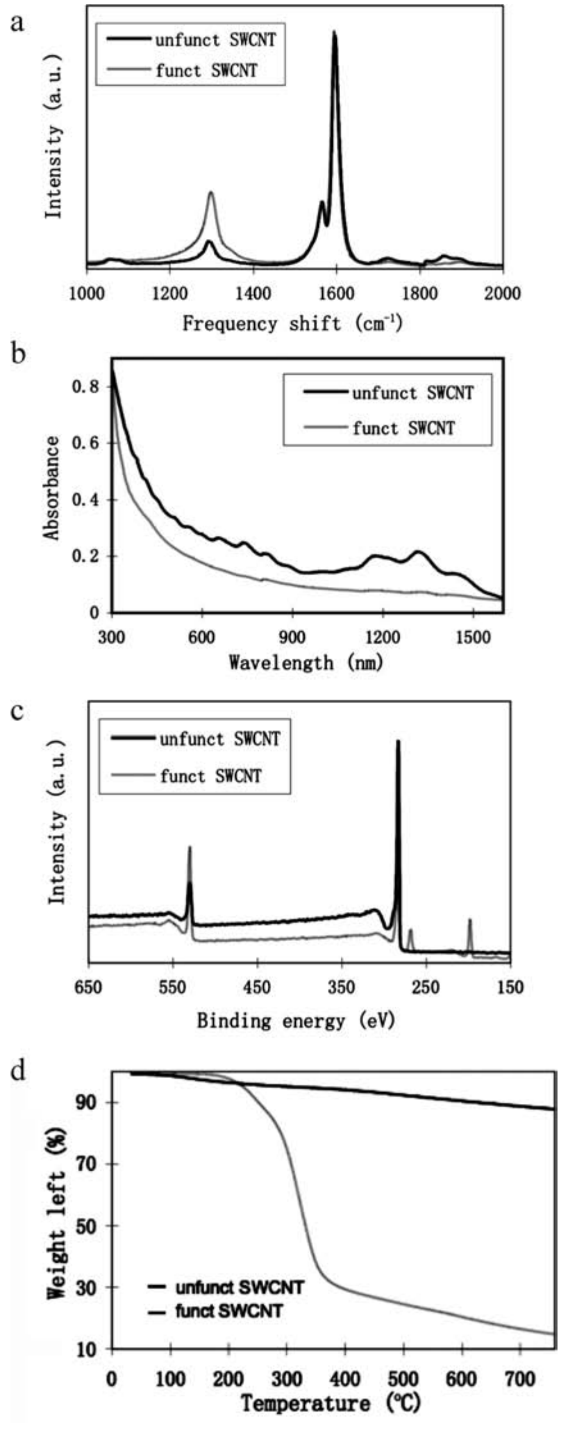


Figure 1. Characterization of chloroethyl-substituted SWCNT derivative **19**. (a) Normalized Raman spectra at 1596 nm, (b) UV−vis−NIR in DMF, (c) XPS of pristine and functionalized SWCNTs, and (d) TGA of pristine and functionalized SWCNTs.

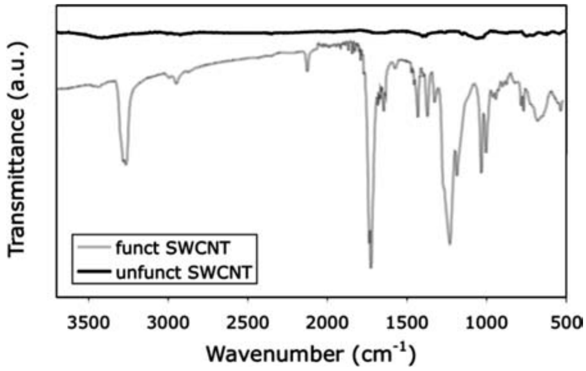


Figure 2. IR spectrum of propargyl-substituted SWCNT derivative **21**.

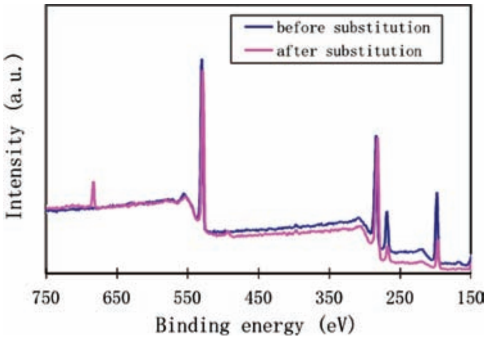
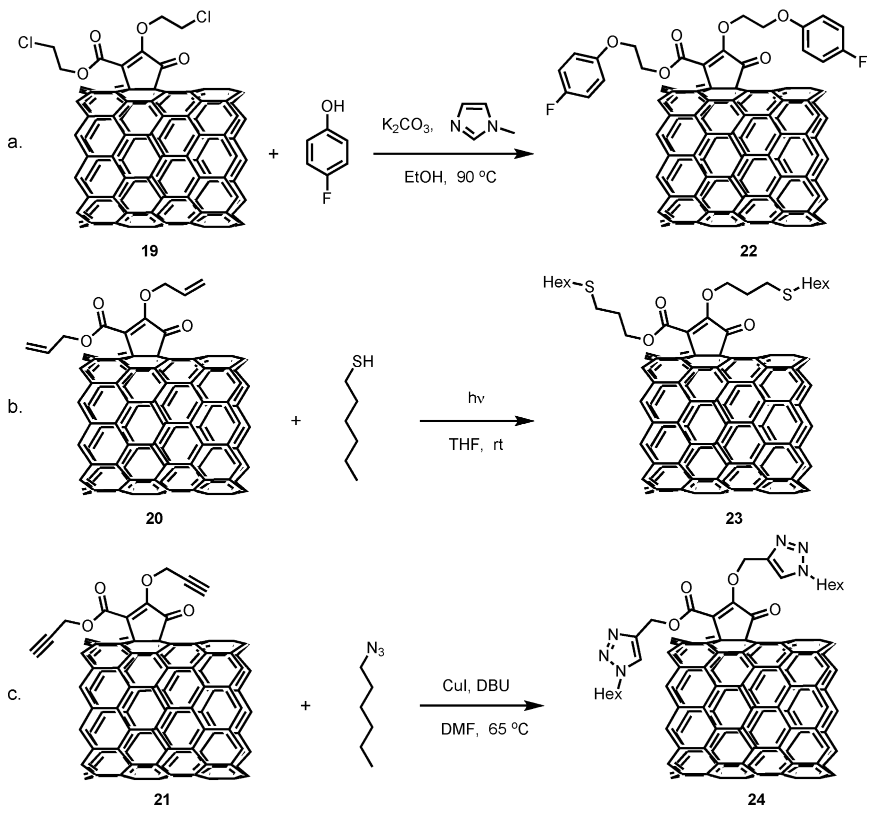


Figure 3. XPS of *p*-fluorophenyl-substituted SWCNT derivative **22**.

SWCNT product **23** was characterized by XPS (Figure 4), which shows the new sulfur peaks at 159 and 230 eV correspond to the S 2p, 2s core-level energies, thereby indicating that a successful addition reaction occurred. The estimated functionalization density is 1 thioether adduct for 45 SWCNT surface C atoms. Finally, we turned our attention to the dipropargyl-substituted SWCNT **21**, which could undergo further chemical transformations including cross coupling[18,19] or 1,3-dipolar cycloaddition (click chemistry).[23] The click chemistry concept, introduced by Sharpless, is ideal for further functionalization of a CNT precursor. We therefore explored copper-catalyzed version of the Husigen's [3 + 2] cycloaddition between the pendant alkynes and azides.[23,31−33] As a proof-of-concept experiment, cycloaddition of 1-hexylazide[33] with the propargyl groups pendant to the SWCNTs was conducted in DMF at 65 °C for 12 h (Scheme 7c). The reaction was catalyzed by CuI with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the base.[34] IR spectroscopy of the functionalized SWCNT reveals almost quantitative conversion of the terminal acetylenes into the expected 1,2,3-triazole cycloadduct (Figure 5). The absorption signals at 2130 cm^{-1} attributed to the C−C stretching mode of the terminal acetylenes and the signal at 3260 cm^{-1} corresponding to C−H stretching of sp carbon are barely observed, indicating the high efficiency of this transformation. Clearly the functionalized SWCNTs (**19**−**21**) serve as versatile precursors for further CNT functionalization to facilitate CNT applications.

Chemical Transformations of Pendant Cyclopentenones. Chemical transformation of the installed cyclopentenone groups represents another precursor-based approach to create new functionalized CNTs. We have investigated demethylation of the DMAD-C$_{60}$ adduct **2** with BBr$_3$ at −78 °C (later warmed to room temperature) and isolated fullerene derivative **25** (Scheme 8). The ^{1}H NMR spectrum confirms the disappearance of the methyl group of the vinyl ether. Treatment of **25** with *p*-toluenesulfonyl chloride produced the tosylated fullerene **28**, which represents an interesting precursor for further C$_{60}$ functionalization. DMAD-functionalized SWCNT **26**[12] was also subjected to the same demethylation conditions. IR spectroscopy of the demethylated product **27** showed the decrease of the band at 1246 cm^{-1} (Figure 6a) corresponding to the vinyl methyl ether groups, thereby indicating that the methyl groups on the vinyl position were successfully cleaved. TGA shows slightly less of weight loss upon heating compared to the starting material (Figure 6b), also consistent with removal of methyl

Scheme 7. Functionalization of CNTs from Well-Defined Precursors (a) via S_N2 Reaction, (b) via Thiol Addition, (c) via Click Chemistry



groups. Interestingly, the decomposition temperature (removal of the functional groups from the SWCNT surfaces) is nearly 80 °C lower than that before demethylation. One plausible explanation for this lower stability is the higher strain generated in the cyclopentenone ring through enol-ketone equilibrium (Chart 2). The ability to defunctionalize SWCNTs at lower temperatures is practically useful because although functionalization is often necessary to process/assemble these materials, the pristine (defunctionalized) materials are often desired for their electronic properties. Current covalent functionalization methods generally require high temperatures (600−800 °C) to regenerate the pristine CNTs,^{29,35} which is not compatible with many substrate materials. The significantly lowered regeneration temperature (175 °C) of the demethylated DMAD−CNT adduct **27** is of specific importance for fabricating devices on plastic substrates.

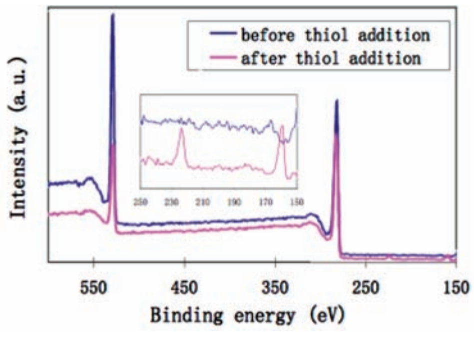
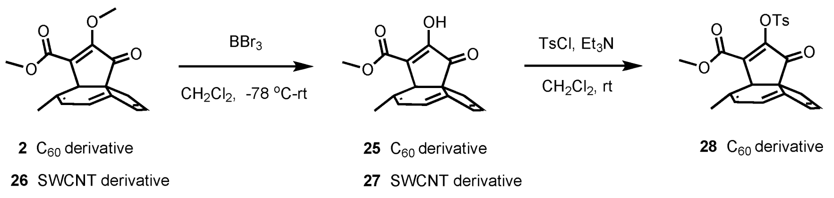


Figure 4. XPS of SWCNT derivative **23** from thiol addition.

Saponification of the ester groups of DMAD-functionalized SWCNTs **26** with aqueous sodium hydroxide solution (0.5 M) at 80 °C afforded hydrolyzed CNT derivative **29** (Scheme 9),^{36} which forms a stable dispersion in water for months (0.5 mg/mL) (Figure S5). Heating pristine CNTs in concentrated sulfuric acid and nitric acid is the most common approach to introduce high density of carboxylic groups onto CNT surface.^{7}However, one disadvantage of this common approach is that CNTs are usually significantly shortened under the harsh conditions and have many defects in their repeating graphene structure. The lowering of the CNT aspect ratio (length to diameter)^{37,38} reduces CNT performance in applications such as electronic devices and CNT−polymer structural composites. In contrast, our two-step (functionalization-saponification) approach creates better-defined CNTs with high density of carboxylate groups.

Large-Scale Functionalization of Multi-Walled Carbon Nanotubes. Given the success in modular functionalization of fullerenes and SWCNTs, we turned our attention to a more challenging target, multi-walled carbon nanotubes (MWCNTs).

Scheme 8. Demethylation of DMAD-Functionalized Fullerene **2** or SWCNT **26**



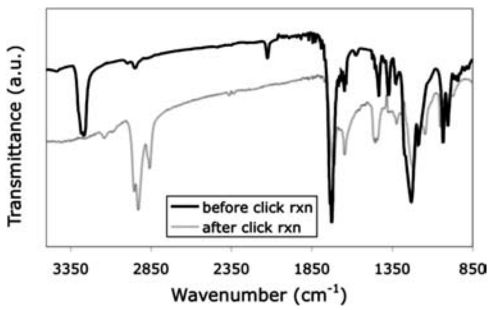


Figure 5. IR spectrum of SWCNT derivative **24** prepared through click chemistry.

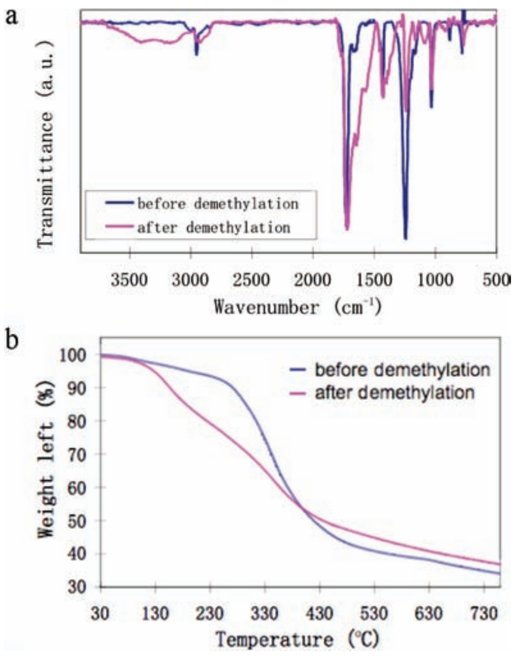
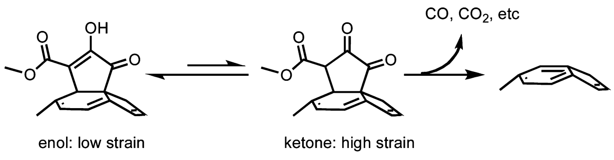
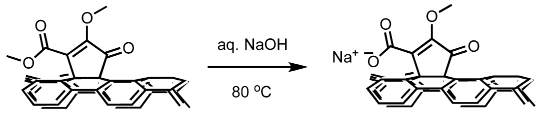


Figure 6. IR (a) and TGA (b) of demethylated SWCNT derivative **27**.

Chart 2. Tautomerization of the Cyclopentenone Moiety: Enol vs Ketone Form



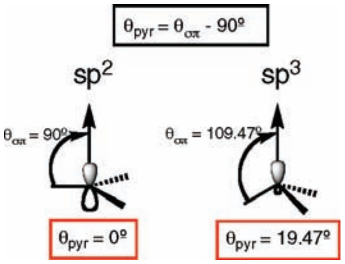
Scheme 9. Saponification of DMAD-Functionalized CNTs



26 SWCNT
30 MWCNT

29 SWCNT
31 MWCNT

Chart 3. Pyramidalization Angles



A common feature of the covalent functionalization of C_{60} and SWCNT is the transformation of an sp^2 to sp^3 carbon atom. Such hybridization change accounts for the driving force for the functionalization reaction.[39] The ideal pyramidalization angle in C_{60} is 11.6°, whereas this angle at an unstrained sp^2-carbon is 0° and increases to 19.47° for sp^3 carbon (Chart 3), so the strain of the fullerene is relieved upon functionalization and the product formation is thermodynamically favored.[40] Even without consideration of π-orbital misalignments, this simple model can explain the lower reactivity of SWCNT compared to C_{60}. SWCNT is bent in only one dimension and its diameter is around 1 nm, which is larger than C_{60}'s diameter (0.7 nm), so the pyramidalization angle of SWCNT is smaller than that of fullerene. Transformation of an sp^2 carbon to sp^3 hybridization is therefore less favored and makes SWCNT functionalization more difficult. All these factors make MWCNT functionalization even more challenging. The diameter of MWCNT (outside tube) is between 20 and 50 nm, thus making the pyramidalization angle smaller than that of a SWCNT. As a result, the covalent functionalization methods reported for MWCNTs usually require harsh conditions, such as strong acid or base, high temperature, high pressure, or long reaction times.[6] However, we hoped that our zwitterion approach would enable highly efficient functionalization of MWCNTs under mild conditions.

MWCNT functionalization was performed under the same reaction conditions as for SWCNT (DMAP as nucleophile, DMAD as electrophile, 60 °C, THF). Characterization of the MWCNT product **30** with IR, TGA, and XPS indicated successful functionalization (Figures S6−S8). After saponification MWCNTs **31** displayed good solubility in a variety of solvents, including water (1.0 mg/mL), ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate, 1.1 mg/mL), and propylene carbonate (1.0 mg/mL), thereby greatly facilitating the processing and manipulation of MWCNT-based composite materials.

To further explore the potential of our zwitterion approach, we sought to demonstrate the feasibility of large-scale functionalization of MWCNTs. Initially the reagent (DMAP and DMAD) loading was optimized using SWCNT as the model substrate due to the fact that covalent functionalization leads to a decrease of the characteristic interband transitions between van Hove singularities of pristine SWCNTs, which can be conveniently monitored by UV−vis−NIR absorption spectroscopy.[28,29] The standard conditions were DMAD and DMAP loadings of 25 and 30 equiv, respectively, per SWCNT carbon atoms, which afford highly functionalized SWCNTs (Figure 7, red line). Decreasing both reagent loadings to 50% or less of the original amounts led to SWCNT products with lower functionalization density (Figure 7, green line). However, changing the solvent from THF to *p*-dioxane and raising the reaction temperature from 60 to 95 °C significantly improved the reaction efficiency (Figure 7, blue line). SWCNT derivatives with similar functionalization density as previously reported under the standard conditions were obtained with 10 equiv of DMAD and 6 equiv of DMAP loading, which represents a significant step toward efficient large-scale CNT functionalization.

In further optimization studies we found that the poor solubility of DMAP in dioxane was another challenge in the large-scale CNT reaction. In our original small-scale procedures, both DMAD and DMAP solution are slowly added to the CNT suspension to minimize side product formation.[12] However, for

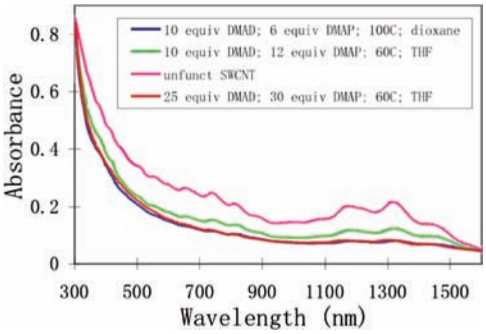


Figure 7. UV−vis−NIR of functionalized SWCNTs in DMF.

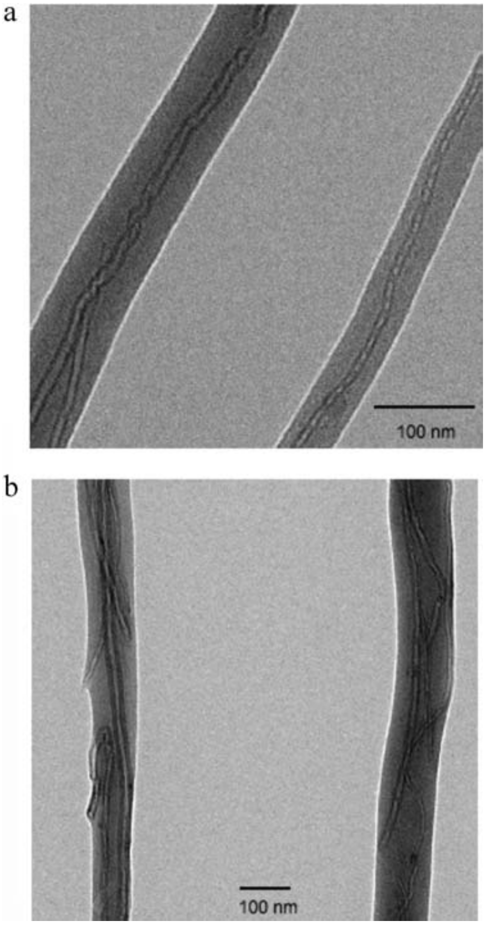


Figure 8. TEM images of MWCNT−PEO electrospun fibers.

a 10 g scale CNT reaction, fully dissolving the DMAP would require more than 1 L of dioxane, which is an impractical condition. To avoid the use of large amount of solvent, DMAP is added in one portion at the beginning of the reaction followed by slow addition of DMAD. However this approach only provided CNT products with low functionalization density. Presumably, in the presence of large amount of DMAP, the binding of DMAP onto CNT surface increases the electron density on CNTs,[41] thus making them poorer electrophiles and less reactive with the zwitterion intermediates. This failure indicates that a slow addition of both reagents is necessary for efficient CNT functionalization. After screening a variety of nonprotonic solvents,[42]we found DMAP showed the highest solubility in chloroform (∼0.65 g/mL), thus avoiding the use of large amount of *p*-dioxane solvent for the purpose of predissolving DMAP. Slow addition of both the DMAP solution in chloroform and DMAD in *p*-dioxane to the MWCNT (10 g) suspension in *p*-dioxane at 95 °C afforded MWCNT derivatives with high functionalization density. TGA characterization of purified MWCNT products showed a weight loss of 28% (Figure S9), corresponding to about 1 functional group for 38 CNT carbon atoms. Upon saponification, the hydrolyzed MWCNT derivatives showed high solubility in water (1.2 mg/mL). This multigram-scale functionalization of CNTs under mild conditions represents a significant step toward commercial-scale production of MWCNT derivatives.

Electrospun Fibers of Water-Soluble CNTs in Poly(ethylene oxide) (PEO). Electrospinning is a convenient and versatile approach to produce polymer nanofibers and their composites.[43] This process involves the production of continuous one-dimensional fibers from an electrostatically driven jet of a polymer solution. In an electric field of several kV/cm, nanofibers are formed by the elongation of the ejected stream and onset of the electrically-driven whipping instability.[43] CNTs are generally treated with strong oxidative acids or surfactants to achieve a dispersions that are stable for extended periods in polar organic solvents (e.g., DMF) required for electrospinning.[44−49] As discussed above, oxidative acid treatment decreases the CNT aspect ratio and introduces defects. Surfactants that are not covalently connected to the CNTs are not always desired as they can diffuse in the composite material. Considering the good solubility in water displayed by hydrolyzed MWCNT derivative **31**, we explored its applicability in the preparation of electrospun fibers from aqueous solutions.

We studied compositions utilizing poly(methacrylic acid) (PMAA) as the polymer component with DMF used as a solubility enhancing cosolvent. The latter was added in an attempt to ensure that the MWCNTs are evenly distributed in

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(36) We cannot completely rule out the possibility that the vinyl methoxy groups (at least some of them) are also replaced by the hydroxy group. A model study by using fullerene derivative as the substrate was also attempted, but due to solubility issues, ^{1}H NMR spectrum acquisition was not successful.

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the final composites. Although SEM image (Figure S10a) showed that composite fibers with a relatively uniform size distribution (diameter around 100−200 nm) were obtained, MWCNT incorporation was low and MWCNTs were absent in some fibers on the basis of TEM characterization (Figure S10b). We obtained better results with PEO as the polymer. Experiments were performed with unfunctionalized MWCNTs (for comparison) in parallel to **31** and equal concentration (MWCNT, 1.0 mg/mL) dispersions in aqueous solutions of PEO were given a brief 5 min sonication. A uniform ink-like black suspension of functionalized MWCNTs **31** was obtained that remained homogeneous under ambient conditions for over a week. As expected, the unfunctionalized MWCNTs did not form a stable dispersion and phase separation occurred quickly within 5 min after sonication. Composite fibers were prepared by electrospinning a MWCNT/PEO composite solution with 5 wt % of MWCNTs. TEM images revealed that the MWCNTs align parallel to the axis direction of the nanofibers (Figure 8a). In some fibers, several CNTs could be aligned side by side in a single polymer fiber (Figure 8b). The uniformity of these fibers and distribution of the MWCNTs is further evidence that the dispersions formed are of high quality, which suggests that these methods have applicability in the preparation of CNT−polymer composites, wherein the quality of the dispersion is critical to give homogenously processed materials.

Conclusions

Highly efficient, zwitterion-mediated approaches have been developed for the modular functionalization of CNTs (both single-walled and multi-walled) and fullerenes. The trapping of charged zwitterion intermediates, generated in the functionalization reaction, with different nucleophiles allows for the installation of a variety of functional groups on the fullerenes and CNTs in a one-pot reaction sequence. The pentafluorophenoxy-functionalized fullerene **13** is a versatile precursor that undergoes substitution reactions under mild conditions. Phenol addition to CNTs was not as efficient, due to the back-attack of methoxide generated during the reaction. However, further functionalization of CNTs is accomplished by reactions with functional acetylenedicarboxylate diesters **15**−**17**. This approach readily yields CNTs substituted with chloroethyl, allyl, and propargyl groups (**19**−**21**), which undergo further functionalization through S_N2 substitution, thiol addition, or 1,3-dipolar cycloaddition (click chemistry). Additional chemical transformations (demethylation and saponification) of the cyclopentenone moieties that are added to the CNTs led to demethylated and hydrolyzed products, and aqueous dispersions (1.2 mg/mL for MWCNTs) are stable for months. Large-scale (10 g) functionalization of MWCNTs was also accomplished demonstrating the potential of this zwitterion approach for bulk production of CNT materials. These approaches enable high functionalization densities of 1 functional group per 10 carbon atoms for SWCNTs.

As an initial demonstration of the potential of these functionalized CNTs to be used in composite materials, we produced MWCNT−PEO nanofibers by electrospinning. The excellent uniformity of the MWCNTs in these fibers is an indication of the effectiveness of our functionalization method. Currently, applications of novel CNT derivatives in chemical sensing, electrocatalysis,[50] and preparation of electroactive actuators and nanocomposites are being explored in our lab and will be reported in due course.

Experimental Section

Materials. Raw (HiPCO) SWCNTs, received from Carbon Nanotechnologies Inc. (CNI lot no. R0204), were further purified by exposure to air at 300 °C followed by concd HCl wash to remove remaining metal catalysts before use. Fullerenes (99.5%) were obtained from Alfa Aesar and Nano-C, Inc. and used as received. MWCNTs were obtained from Aldrich (>95% purity, for small-scale reactions) and Bayer Group (BaytubesC 150 P, >95% purity, for large-scale reactions) and used as received. All solvents were of spectroscopic grade unless otherwise noted. Anhydrous toluene and tetrahydrofuran were obtained using a solvent purification system (Innovative Technologies). All other chemicals were of reagent grade and used as received.

General Information. Nuclear magnetic resonance (NMR) spectra were recorded on Inova-500 NMR Spectrometer. Chemical shifts are referenced to residual solvent. Mass spectra were obtained on Bruker Omniflex MALDI-TOF instrument. Raman spectra were measured on a Kaiser Hololab 5000R Raman spectrometer using the excitation wavelength of 785 nm. The spectra in the UV−vis−NIR range were obtained using a Cary 6000i UV−vis−NIR spectrometer. TGA analyses were performed with a TGA Q50 apparatus (TA Instruments). Experiments were carried out under nitrogen. Samples were heated at 5 °C/min from 30 to 800 °C. FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrometer by drop-casting the material on a KBr disk. XPS spectra were recorded on a Kratos AXIS Ultra X-ray photoelectron spectrometer. All synthetic manipulations were carried out under an argon atmosphere using standard Schlenk techniques unless otherwise noted. Glassware was oven-baked and cooled under N_2 atmosphere.

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Supporting Information Available: Preparation procedures, kinetic data on fullerene substitution reactions, characterization data for CNT derivatives, and SEM and TEM images of MWCNT−PMMA electrospun fibers. This material is available free of charge via the Internet at http://pubs.acs.org.

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